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13. ABSTRACT (Maximum 200 words)

The goal of this project was to utilize weakly coordinating anion technology to produce new materials for use as proton conducting electrolytes. The main focus of the work was to be protonated arene ionomers. The protonated arenes have not met the requirements of thermal stability and proton conductivity. Continuation of the research effort on a more fruitful class of materials has led to a wide range of compounds based upon WCAs that have been shown to be applicable to some of the problems facing proton conducting electrolytes. A number of thermally stable materials have been generated with mild proton conductivity, but temperature ranges up to 400°C. Materials based upon hydroxylated boranes appear particularly promising due to similarity in basicity to water. Application of these materials as water surrogates may enhance current proton conducting materials.

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Protonated arenes as solid proton conducting electrolytes.

Table of Contents

Statement of the problem studied:

The desire for fuel cell systems that operate at elevated temperatures are one of the driving forces for research in a wide range of areas. The higher temperatures required stem from the ability to use less costly metals for the electrocatalysts that make up the electrolyte/electrode assemblies, improve conductivity of the electrolyte and provide favorable reaction kinetics at the electrodes themselves.(Kreuer 1996) One class of materials receiving much attention are the polymer electrolytes membrane systems (PEMs).(Steele and Heinzel 2001) The difficulty that arises in these materials is that prime operating conditions for small-manpowered units are temperatures in the 80-200°C range and in general the electrolytes utilized, acidified proton conducting ionomers, rapidly dehydrate above 100°C and become resistive. While humidification of the fuel stream can restore this lost conductivity, this adds to the mass, cost and complexity of the device. New materials that have favorable ion transport mechanisms, high thermal stability, low moisture requirements, and provide low ohmic loss need to be generated and allow for higher operation temperatures.

The acidified ionomers that make up most proton conductors are generally based upon simple oxyanions such as sulfates, phosphates, and carbonates.(Norby 1999) More exotic anion systems such as fluorinated nonmetals (SbF_6^-, etc) have not been utilized because of poor thermal stability and lack of synthetic flexibility. Advances in anion technology have lead to the generation of an extremely robust class of anions that have high thermal stability, low nucleophilicity and low basicity. These anion systems, often described as weakly coordinating anions (WCAs) are among the most stable class of anions know (Fig. 1).(Strauss 1993) Typical examples of weakly coordinating anions are
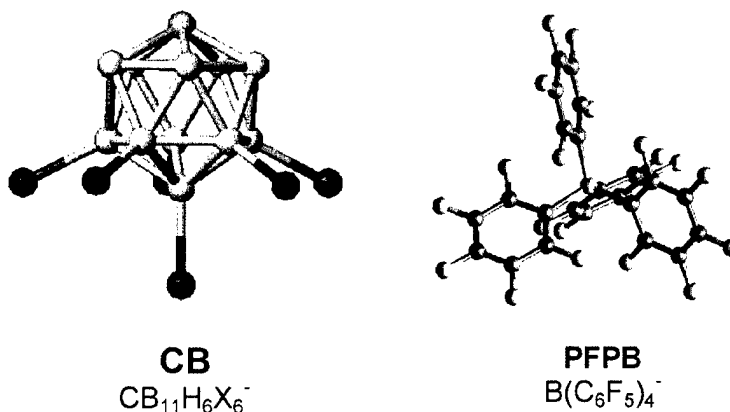

CB

$CB_{11}H_6X_6^-$

PFPB

$B(C_6F_5)_4^-$

Fig. 1. Typical weakly coordinating anions, carboranes (CB)
and perflourinated phenyl borates (PFPB)

perfluorinated aryl borates (BAr_F^-) and the derivatized polyhedral carborane and borane anions such as $CB_{11}H_6Br_6^-$. (Reed 1998) The carboranes and boranes are particularly well suited for use in proton conducting electrolytes due to high acid stability. These anion systems, when paired with suitable cations, can act as super-acidic media.(Reed, Kim et al. 2000) One of the tenets of this research is to explore the application of these robust anion systems to protonic conducting materials.

There are three classes of molecules that are of interest for utilization in PEM and other proton conducting materials that result from interaction with WCA compounds. The first, and the original focus of this research project, are the protonated arenes that result

2

from direct acidification of a π-system. These protonated arenes or areniuim ions in some cases are super acidic and have been shown to have rapid inter- and intra- molecular proton exchange.(Reed, Kim et al. 2003) Another system of interest is the hydronium ions, protonated water clusters that have been shown to be key intermediates and transition states in a wide range of PEM materials, also these materials were examined because they are likely to be one of the leading contaminants resulting in the decomposition of protonated arenes. Lastly, anhydrous proton conducting materials based upon hydroxylated boranes were discovered and their properties examined.

Summary of the Most Important Results:
Protonated Arenes stabilized by WCAs:
Protonated arenes are an exotic class of molecules often thought to be unstable at higher temperature (Fig 2). Recent work has shown that this is not the case when the reactive cations are paired with carborane based anions.(Reed, Fackler et al. 1999) This has allowed for the isolation of arenium ions in high yield, even the superacidic protonated benzene molecule.(Stasko and Reed 2002) It was believed that the above mentioned high
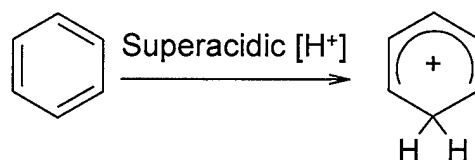

Fig. 2. Synthesis of protonated arenes such as $C_6H_7^+$

proton mobility observed in the case of simple arenes could be extended to larger arene frameworks. The net effect of the extension of the π-system would be to increase the electron density. This would have two main effects: increasing the basicity of the π-system and increasing the stability of the arenium ion generated upon protonation.

To test this hypothesis several protonated arene systems were examined: arenium ions based upon toluene, anthracene and phenanthrene. These systems were chosen for ease of synthesis and in the case of anthracene and phenanthrene, because they were readily avalible and solid (Fig. 3). The protonated toluene was generated and isolated according to literature procedure using the hexabromocarborane as a counter ion. This involves generating highly active protons in the reaction of an acid such as triflic acid with a latent silylium cation. These high activity protons then react with the toluene present which is the lowest basicity substance in the media, forming the tolueneium. The toluenium was isolated in high yields (<80%) as a yellow crystalline solid. Production of the other arenium ions was accomplished according to modification of literature procedure utilizing two different methods. The first was direct reaction of latent sliylium
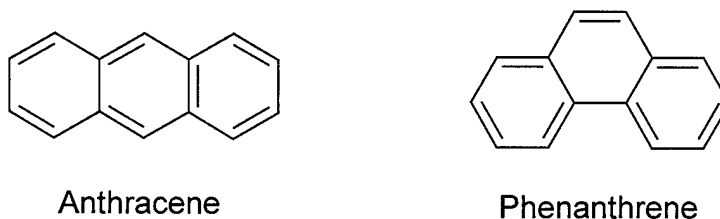

Anthracene   Phenanthrene

Fig. 3. Substrates for arenium ion formation utilizing the $CB_{11}H_6Br_6^-$
counter ion

3

cations with triflic acid in the presence of the arene as described above. The materials were isolated as an orange solid in the case of anthracenium ion and a brown-green solid in the case of phenanthrene.

Unfortunately the stability of the protonated arenes was far less than desired in either the solid state or the solution state. While protonated arenes such as pyrene have shown good stability in super acid media, few examinations in other solvents have been undertaken. The material, upon isolation will quickly decompose (hours in solution, one day as solid). Despite the stability of the more acidic protonated toluene, the phenanthrenium and anthrecenium do not persist. Spectroscopic evidence suggests that the arenium ions are undergoing nucleophilic decomposition. In arene solvent such as benzene, it appears that the materials become arylated. While nucleophilic attack by an arene is not standard, there are a number of examples reported where arylation of carbocations is observed. In particular, extended π-systems such as anthracene and related systems can undergo dimerization.(Laali, Okazaki et al. 2002) The process takes place upon partial deprotonation which can be produced in a large number of fashions. The expected need for some amount of deprotonation in an active fuel cell system limits the applicability of these materials. Other cases of arene nucleophilic attack are seen in curved π-systems such as fullerenes which rapidly arylate in the presence of arene solvents and proton sources.(Olah, Bucsi et al. 1991) Switching to more highly substituted arenes may allow for generation of systems of greater stability. Unfortunately, with this strategy, a potential degradation pathways is oxidation to the dication followed by proton loss. Protective alkylation of the arene rings will only increase this tendency to undergo oxidation. This redox instability and unexpected reactivity limits the material choices. Unfortunately the application of protonated arene systems to proton transfer materials is currently not feasible. While simple aromatic systems (single or 2 ring aromatics such as protonated benzene or protonated naphthalene) may be easily isolated using weakly coordinating anions, extension of this chemistry to larger π-system frameworks is currently hampered by secondary reactivity and low overall stability.

Hydronium, Oxonium and Hydroxylated Boranes:

Despite the failure of the main research focus of the proposed work, additional parallel avenues provided a range of new opportunities. In addition to protonated arene compounds, the utilization of hydronium ion (H_3O^+, $H_5O_2^+$ and $H_9O_4^+$) salts of weakly coordinating anions was also examined.(Lundgren and Olovsson 1976) These materials have been proposed to act as intermediates and proton carriers in many solution and solid state systems.(Eikerling, Paddison et al. 2003) These systems were found to have a number of examples in the literature though there were very few thermally stable varieties owing to the high reactivity of the oxonium ion. Two initial compounds were selected for study, the $H_9O_4^+$ salt of $CB_{11}H_6Br_6^-$ and what was described (incorrectly) in the literature as solid salt of a hydronium ion, $(H_3O^+)_2B_{12}(OH)_{12}$.(Xie, Bau et al. 1995; Peymann, Knobler et al. 2001) Both sets of compounds were easily prepared from literature procedures and examined for proton conductivity. It was found initially that the $H_9O_4^+$ salt had a low conductivity of approximately 10^{-6} S/cm but showed rapid increase in conductivity to 10^{-4} S/cm until approximately 80°C (Fig. 4) The conduction process was found to have an activation enthalpy of ~15 kcal/mol (0.64 eV). The change in
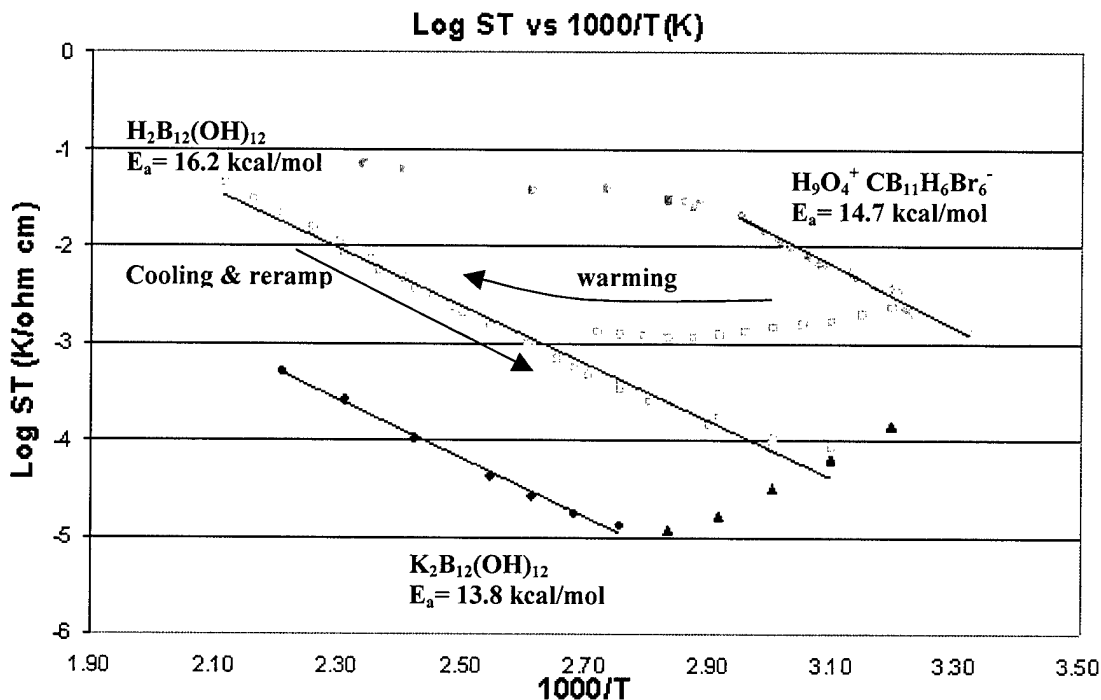
4

Log ST vs 1000/T (K)

Fig 4. Arrhenius Plot of Conductivity Data for a number of proton conducting materials:
$H_9O_4^+$ $CB_{11}H_6Br_6^-$, $H_2B_{12}(OH)_{12}$, and $K_2B_{12}(OH)_{12}$

conductivity was due to the conversion of the $H_9O_4^+$ cation into the $H_5O_2^+$ cation via water loss. This water loss was quantified and the thermal decomposition utilized to access the $H_5O_2^+$ cation directly. This represents the first large scale preparation of the $H_5O_2^+$ cation and work is currently underway to examine the bonding within this molecule through the use of electron density measurements obtained from high resolution X-ray crystallography. The distinct hydrogen bonding pattern leads to strong, short hydrogen bonding interactions as evidence by two distinct infrared markers: a sharp O-H stretch of the external O-H bonds and a broad low energy absorbance centered at 1600 cm^{-1} that corresponds to the O-H-O bond vibration.(Stasko, Hoffmann et al. 2002) This material was found to be stable to about 200°C where it loses another water molecule to become the H_3O^+ cation, this also represents one of the first bulk methods of generating large quantities of the oxonium ion (H_3O^+) paired with WCA materials.

The above experiments show that proton conducting materials can be generated utilizing nontraditional anion systems such as carboranes in conjunction with suitable cations. The temperature limitations of the hydronium salts ($H_5O_2^+$ and $H_9O_4^+$) prevent their direct application except as academic curiosities. The limitation of the oxonium (H_3O^+) due to its unimolecular nature and absence of hydrogen bonding media would appear to restrict proton migration to a vehicle mechanism, though investigation into the proton conducting properties of this cation with the $CB_{11}H_6Br_6^-$ anion was not undertaken. The vehicle mechanism would not be favorable for conventional fuel cell systems due to dehydration effects and the development of a water gradient in the electrolyte. Therefore, other hydrogen bonding environments were explored that could allow for Grotthus-style proton transfer. To this end two alternative anion systems were explored, the $B_{12}(OH)_{12}^{-2}$ material mentioned above, and a new anion system that would

5

combine hydrogen bonding ability with low over all basicity, mixed halo-hydroxy carboranes, of which $HCB_{11}(OH)_5Br_6^-$ would represent the first example. The carborane and borane cage structure is extremely robust and capable of substantial alteration. Even though the boron oxygen bond is one of the strongest known, the closed borane and

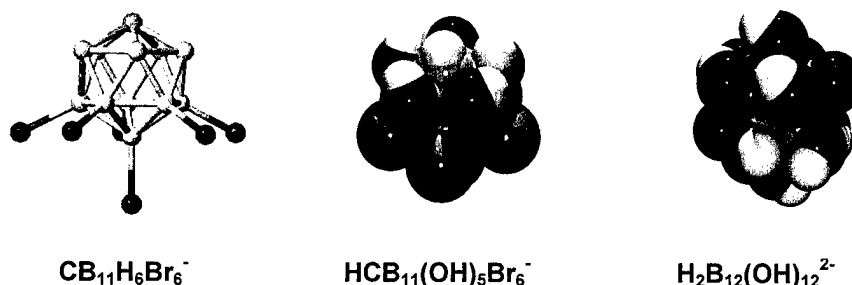$CB_{11}H_6Br_6^-$ $\qquad$ $HCB_{11}(OH)_5Br_6^-$ $\qquad$ $H_2B_{12}(OH)_{12}^{2-}$

Fig. 5. A selection of the robust anions utilized during the course of this research.

carborane cages resist oxidative degradation, even in the presence of oxygenating agents like hydrogen peroxide.(Peymann, Herzog et al. 1999) This stability can be harnessed and allows for the isolation of the mixed halo-hydroxy carborane $HCB_{11}(OH)_5Br_6^-$ and the completely hydroxylated B_{12} cage compound $B_{12}(OH)_{12}^{-2}$. The mixed halo-hydroxy anion could be manipulated in many ways like the halogenated carborane and could be readily converted to the corresponding $H_9O_4^+$ salt by simple activation with an ion exchange resin. Additionally, thermal conversion of the $H_9O_4^+$ $HCB_{11}(O H)_5Br_6^-$ results in the formation of the $H_5O_2^+$ salt. This affords the opportunity to examine this rare cation in two very different environments: hydrogen bonding and non-hydrogen bonding. The poly-hydroxylation does not significantly alter the basicity of the cage with respect to the $H_9O_4^+$ cluster, but the new anion shows a greater basicity towards the $H_5O_2^+$ cation. This can be rationalized by comparing temperatures at which water loss occurs in the case of each anion. Both the hydroxylated and nonhydroxylated carborane cage show a transition from the $H_9O_4^+$ cation to the $H_5O_2^+$ cation at 80°C. Another interesting result is that the mixed halo-hydroxy anion appears to accept the proton from the $H_5O_2^+$ cation much more readily than the unhydroxylated version. While the infrared spectrum of the $H_5O_2^+$ cation remains relatively unperturbed, upon warming to 150°C there is loss of both remaining water molecules with subsequent proton transfer to an anion hydroxyl group giving the zwitterionic protonated carborane. This result suggests two things: that the degree of solvation of the hydronium ion alters its overall acidity, and that there can be reversible proton transfer to the hydroxylated cage depending on the degree of solvation.(Farcasui and Hancu 1997) Under near anhydrous conditions or higher temperature, the proton would reside on the cage framework, solvated by anion hydroxyl groups and at lower temperatures water or other materials could act as the proton acceptor.

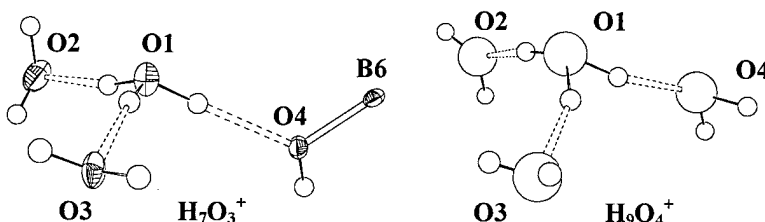Additional work was done to examine the basicity of the mixed halo-hydroxy

Fig. 6. Comparison of the geometry of the $H_7O_3^+$ cation from mixed salt with the previously reported $H_9O_4^+$ cation.

anion. The anion was found to have a basicity very similar to that of a water molecule, readily stabilizing protons in the form of hydronium ions. A wide range of hydronium ions based upon mixed salts were isolated that had the general form $H_3O^+(H_2O)_nHCB_{11}(OH)_5Br_6^-$ · AX (Where A and X denote an inert salt). One of the more interesting cases is the mixed salt $H_3O^+(H_2O)_2$ / $MePPh_3^+$ $(HCB_{11}(OH)_5Br_6^-)_2$ · $3H_2O$. This material represents one of the rare examples of the $H_7O_3^+$ cation, which can be thought of as an intermediate between the $H_9O_4^+$ cation and the $H_5O_2^+$ cation. The similarity of the hydroxylated anion to water molecule can be seen in the preferential orientation of the $H_7O_3^+$ cation into an arrangement that is highly reminiscent of the $H_9O_4^+$ cation (Fig. 6). Additionally, examination of the arrangement of anion hydroxyl groups, hydronium ions and coordinated water molecules shows many structural features that mimic the hydrogen bonding environment found in hexagonal ice (Fig. 7). While this ice-like structure is fragile and deliquescent, it helps to illustrate some of the similarities between water molecules and the hydroxylated frameworks that may serve as water surrogates in nonaqueous PEM systems.(Ma, Wainright et al. 2003)
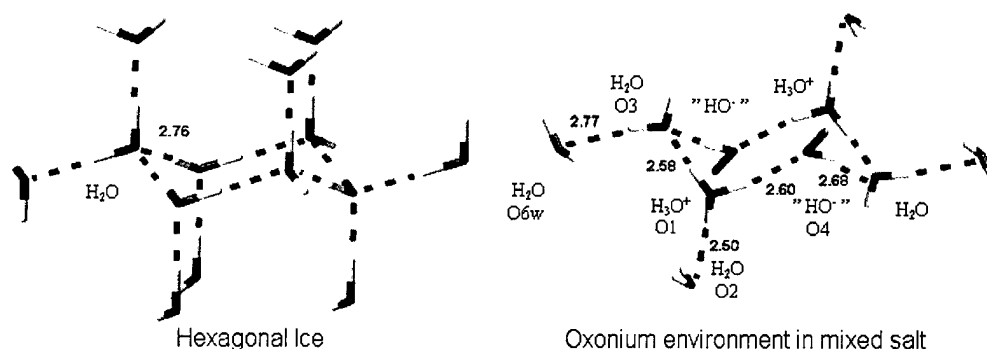

Hexagonal Ice   Oxonium environment in mixed salt

Fig. 7. Comparison of I_h-Ice and coordination environment of $H_7O_3^+$ cation found in certain mixed salts of the halo-hydroxy carborane.

A related set of materials based upon the $B_{12}(OH)_{12}^{2-}$ anion were also examined due to the literature report of a material identified as the H_3O^+ salt of the hydroxylated borane cage. Our desire to examine the influence of environment on proton transport ability and the high proton activity normally observed in the presence of the oxonium led us to this set of compounds. Initial examination of the proton conductivity of the literature material revealed a low conductivity with a negligible increase in the conductivity as a function of temperature. Unfortunately this material was ill defined and found to have behaviors inconsistent with the formulation as $(H_3O)_2B_{12}(OH)_{12}$. This compound was formed by acidification of salt solutions of the hydroxylated dianion and resulted in an insoluble powder. Examination by powder X-ray diffraction and TGA/DTA showed that the material contained more than one component and did not have the described composition. The exact nature of the material was elucidated through structural comparison with two salts that would mimic the size and/or hydrogen bonding nature of an oxonium. These two materials, $(NH_4)_2B_{12}(OH)_{12}$ and $K_2B_{12}(OH)_{12}$, were shown to be isostructural to one another but structurally quite distinct from the major component of the questionable oxonium (Fig. 8). Generation of new synthetic methods

7

led to the generation highly crystalline samples of the acidified anion. Structural analysis of this material showed that it was not an oxonium at all. Instead, it was determined that the material was actually the conjugate acid of the hydroxylated anion frame work, $H_2B_{12}(OH)_{12}$. This material resulted in the direct protonation of the $B_{12}(OH)_{12}^{2-}$ framework. This was seen at high temperature in the case of the hydroxylated carboranes, but either due to the high degree of hydrogen bonding or the inherent higher
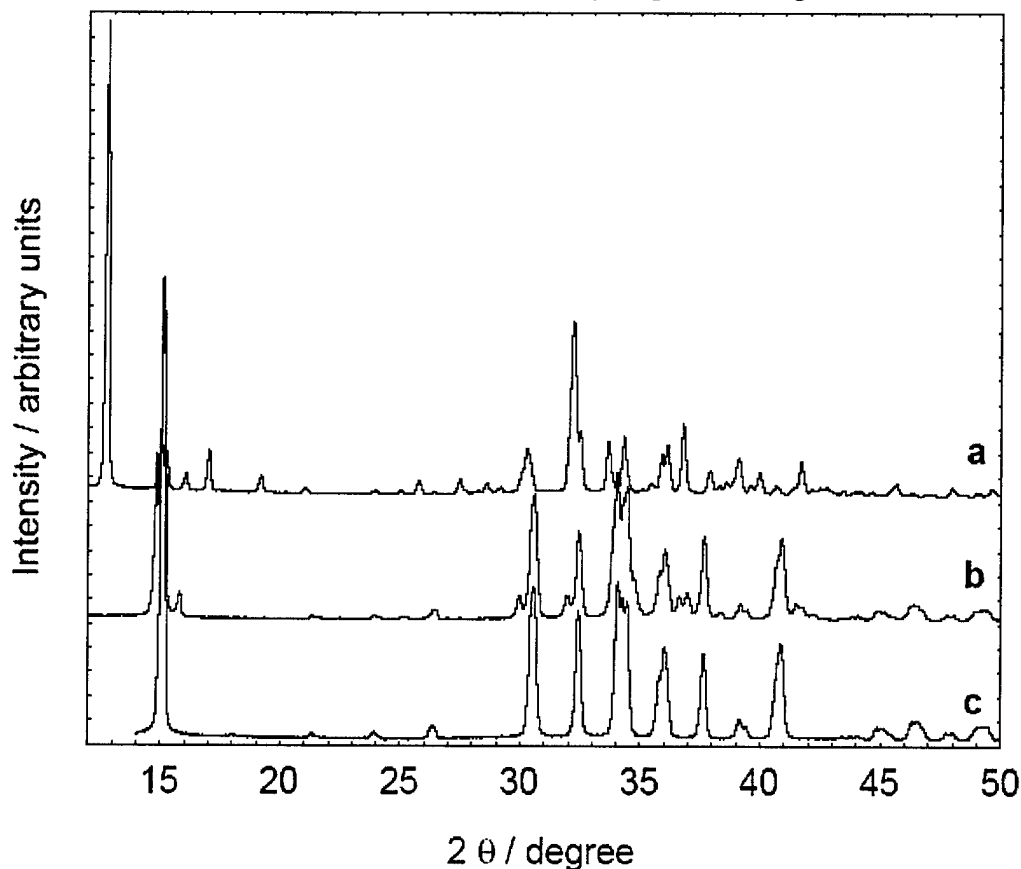

Fig. 8. X-ray powder diffraction data for hydroxylated borane compounds. a) $(NH_4)_2B_{12}(OH)_{12}$
b) crude $H_2B_{12}(OH)_{12}$ from solution route c) $H_2B_{12}(OH)_{12}$ prepared with hydrothermal methods

basicity of a dianionic compound, the $B_{12}(OH)_{12}^{2-}$ anion could be found to be protonated easily in aqueous solution at room temperature. This ready protonation and acidity makes the material more akin to other oxoacids such as sulfuric and phosphoric acid and continued effort to exploit this similarity is underway. One of the major differences between phosphate and sulfate based materials is that this acidic compound is stable to 400°C in the presence or absence of air. Utilization of solid state characterization in the form of powder diffraction clearly showed that the major component formed in the powder production was preferentially formed in the hydrothermal synthesis (See Fig. 8b).

The marriage of powder diffraction, single crystal diffraction, solid state NMR and electrochemical characterization has provided a number of insights into the proton transport process found in these materials. Crystallography shows clearly that these are anhydrous materials, that they are not hygroscopic, though ambient moisture can lead to improved conductivity in the solid state. The crystal structure of $H_2B_{12}(OH)_{12}$ shows a intricate three dimensional hydrogen bonding network, though the bulk of the hydrogen

8

bonds, in particular the eight short-strong hydrogen bonds formed take place within one plane of molecules that runs throughout the crystalline lattice (Fig. 9). The activation energy for the proton conductivity process is essentially identical to that observed for the $H_9O_4^+$ carborane systems and, surprisingly, the nonacidic potassium salt. This evidence, in light of the structural evidence, suggests that a proton hopping mechanism is in effect in all cases and that the anion (in the case of the $B_{12}(OH)_{12}^{2-}$) is serving as the migration site.

The nature of the system also suggests that increasing the number of defects (proton vacancies) will lead to an increase in the conductivity. Part of the evidence for this is seen in hysteresis in the heating cycle. Initial runs of freshly prepared samples, while containing no observable water by DSC or TGA, produce a much higher proton conductivity that wanes as the temperature increases, becoming linear again around 80°C. this is not observed on subsequent runs unless exposed to moist atmospheres for several hours. Variable temperature powder x-ray diffraction also confirms that there is no phase change within the temperature range of the measurements. The surface moisture acts to

● B
○ O
○ H
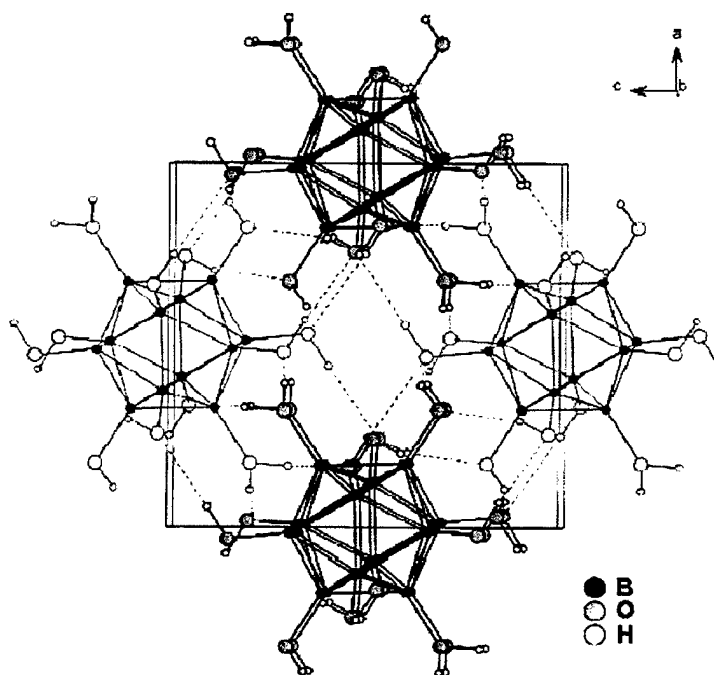
Fig. 9. $H_2B_{12}(OH)_{12}$ Hydrogen Bonding Array

introduce a small number of defects and alter the proton conductivity of the bulk material. This can also be seen through the use of solid state proton NMR. Line shape analysis shows that more than one proton environment is encountered and that there is a low energy process that leads to relaxation at temperatures below the observed 'break' in conductivity of fresh samples. After this temperature, motional narrowing of the resonance more closely resembles the high temperature features seen in the conductivity measurement. The potassium salt, which is also anhydrous shows a similar thermal hysteresis (See Fig. 4). Initial attempts at processing to produce systematic defects through the introduction of other cations into the acidic compound have not yet produced the desired materials, though work is still ongoing. Solution processing of the insoluble

9

crystalline $H_2B_{12}(OH)_{12}$ with the more soluble $K_2B_{12}(OH)_{12}$ salt led to the production of a mixed proton/potassium compound. Unfortunately powder diffraction and SEM revealed that this material consisted of a heterogeneous mixture of the two compounds. Conductivity measurement of the compound showed no improvement in the properties. Alternative strategies are incorporation of imidazole bases or phosphates. One of the more exciting results is high temperature treatment (250°C) of finely ground $H_2B_{12}(OH)_{12}$ with an equimolar amount of H_3PO_4 for 30 minutes produces a new material that shows the highest proton conductivity yet measured for these materials (10^{-3} S/cm @ 227°C).

Efforts are ongoing in the examination of this new class of materials. The similarity between the large polyhedral borane and the small phosphate anion have probed the use of zirconium as well as several other metals to aid in improving the structural stability of the material, introduce defects, and also explore potential overlap between ceramic-like materials and proton conductors. These systems show the ability to include a range of metal ions and a number of crystalline, cesium/zircona materials have been generated. These systems show poor conductivity but offer the potential to be acidified through ion exchange.
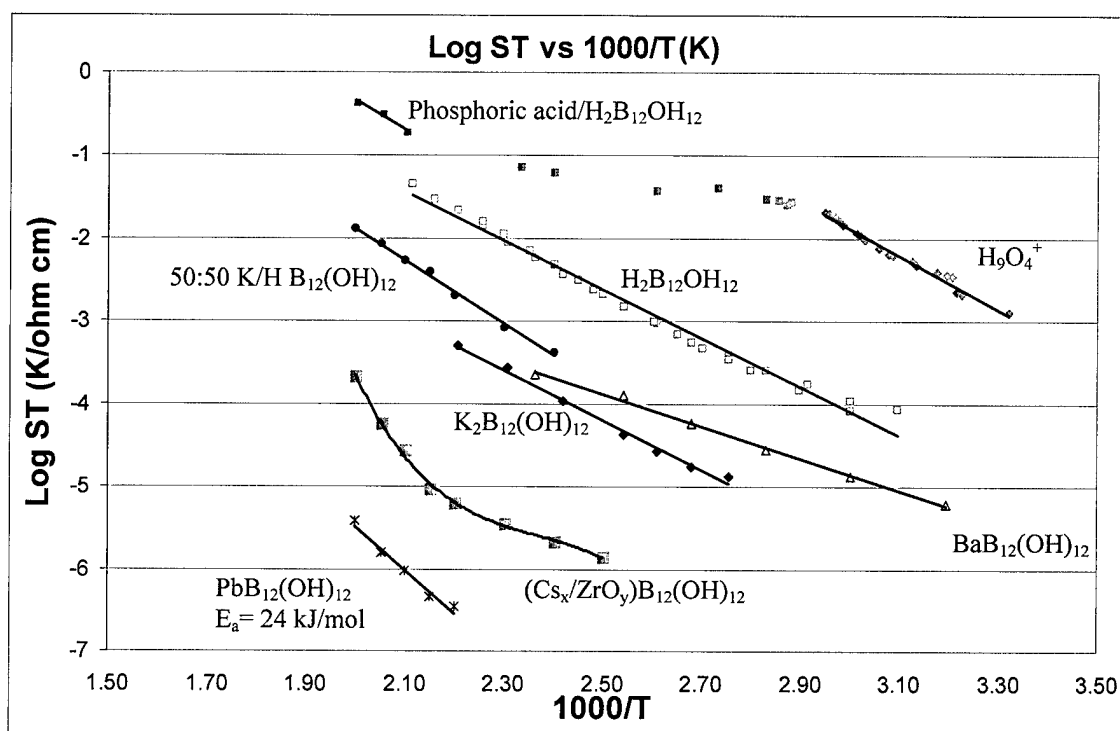

Fig 10. Summary of conductivity data for a selection of the compounds studied.

In summary, while protonated arenes have not met the requirements of thermal stability and proton conductivity, a wide range of other materials based upon WCAs have been shown to be applicable to some of the problems facing proton conducting electrolytes. A number of thermally stable materials have been generated with mild proton conductivity, but temperature ranges up to 400°C. Materials based upon hydroxylated boranes appear particularly promising due to similarity in basicity to water. Application of these materials as water surrogates may enhance current proton conducting materials. Additional work will continue on improving the properties of the materials discussed and generating working PEM assemblies.

Listing of all publications and technical reports supported under this grant or contract.

(a) Papers published in peer-reviewed journals

Stasko, Daniel J.; Perzynski, Kevin J.; Wasil, Mark A.; Brodbeck, Julia K.; Kirschbaum, Kristin; Kim, Yong Wah; Lind, Cora. "An Addition to the Oxoacid Family: $H_2B_{12}(OH)_{12}$." Inorganic Chemistry (2004), 43(13), 3786-3788

Stasko, Daniel J.; Perzynski, Kevin J.; Wasil, Mark A. "Mixed halo/hydroxy carborane anions: thermally stable platforms for hydronium ion isolation." Chemical Communications (2004), (6), 708-709.

(b) Papers published in non-peer-reviewed journals or in conference proceedings

Stasko, Daniel. "New carborane derivatives: Pentahydroxy hexahalo carborane anions." Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, 2003

Stasko, Daniel. "Solid-state conductivity of hydronium salts based upon polyhedral borane and carborane anions." Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, 2003

(c) Papers presented at meetings, but not published in conference proceedings

None.

(d) Manuscripts submitted, but not published

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(e) Technical reports submitted to ARO

None

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Report of Inventions

None

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